Journal of Chromatography, 109 (1975) 67–72

CHROM. 8226

COMPARATIVE GAS CHROMATOGRAPHIC ANALYSIS OF NARCOTICS

III. PHENMETRAZINE HYDROCHLORIDE

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(Received December 9th, 1974)

SUMMARY

Chemical signatures of phenmetrazine hydrochloride were studied by gas chromatography. The inter-batch variations of the signatures were found to be large whereas the intra-batch variations were usually small. The method is used for the tracing of seized phenmetrazine hydrochloride samples to common sources, which in turn may permit further tracing back to chains of illicit distribution of this drug. The applicability of the method to other narcotics is also discussed.

INTRODUCTION

In the first and second parts of this series, gas chromatography (GC) of minor components of hashish[1] and of trace impurities in amphetamine sulphate[2] respectively, was described. The gas chromatograms obtained represent chemical signatures of these drugs. It was found that these signatures could be used for the tracing of drugs, seized by the authorities, to common sources. Assignment of seized street heroin to common sources based on GC analysis of the main constituents was suggested by Shaler and Jerpe[3] but the full results of their experiments seem not to have been published. In the present communication, studies of the chemical signatures of phenmetrazine hydrochloride samples are reported.

Under certain conditions the method may also be applied to other narcotics. These conditions, discussed below, concern the stability of the main constituents and the variation in the chemical signatures.

EXPERIMENTAL

Chemical signatures used for the tracing of samples to common sources should comprise a large number of trace components[2]. It was found that phenmetrazine hydrochloride signatures which meet this requirement could be obtained under the same experimental conditions as in the case of amphetamine sulphate, *i.e.*, extraction of the trace components with benzene from a slightly acidic water solution of 0.5–1.0

g of the sample, concentration of the extract to a small volume followed by GC with flame ionization (FID) and electron capture detectors (ECD).

In order to get useful signatures of other narcotics the experimental conditions may have to be modified. For the extraction of the trace components the solvent giving the maximum number of peaks in the signatures should be selected. As pointed out in Part II (ref. 2), extraction of the trace components into the organic layer has to be carried out in such a way that most of the main component is left behind in the aqueous layer. Tertiary nitrogen compounds such as phendimetrazine, morphine and heroin are weak bases and acidification of the aqueous layer is needed to achieve the desired effect in such cases.

As far as the column temperature programme is concerned, the initial temperature should not be lower than about 130° since the signatures would otherwise include light components which are susceptible to losses in the evaporation step. A straight temperature programme (constant rate) is preferable, since in this type of analysis good reproduction of retention times is more important than complete separation. Higher final temperatures than those used in this study may sometimes be needed for the elution of heavy components. In this case the final temperature (260°) was limited by the ECD used.

Since temperature programming is used in combination with high sensitivity settings (attenuation about ×50) some special precautions are necessary. The gas chromatograph should be run overnight at the final temperature to allow stabilization

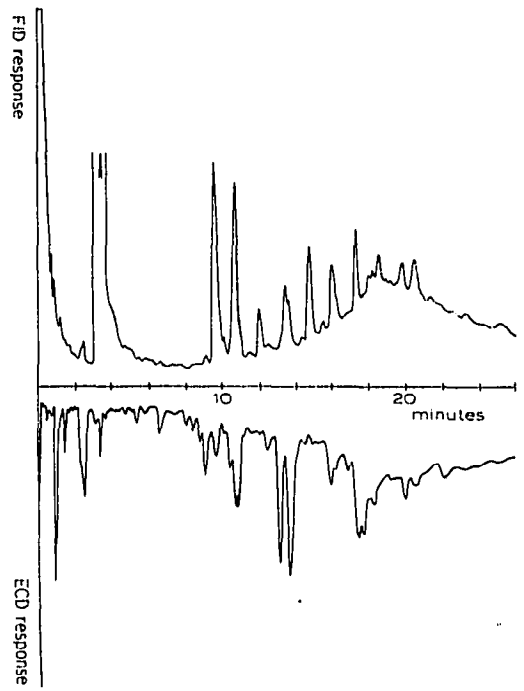

Fig. 1. Chemical signatures of seized phenmetrazine hydrochloride. The peak appearing in the FID signature at 3.6 min is due to a small portion of the main constituent being extracted together with the trace components.

to occur. The analyses should be carried out in one series the following day, beginning with one temperature programme without injection in order to check for ghost peaks. The chemicals used for extraction should be tested from time to time by running blanks.

RESULTS AND DISCUSSION

GC analyses of seized phenmetrazine hydrochloride samples demonstrated that these contain numerous trace impurities as shown in Fig. 1. It may be assumed that these impurities originate essentially from side reactions occurring during synthesis, and from the starting material. This assumption is supported by the results of the amphetamine syntheses reported in Part II (ref. 2).

The results of the analyses mentioned above revealed further that the intra-batch variations of the signatures of seized phenmetrazine hydrochloride were small compared to the inter-batch variations. The prerequisite for the tracing of samples to common sources then concerns the stability of the main constituent as discussed in Part II.

In order to investigate this stability, three samples from a homogenous batch of phenmetrazine hydrochloride recrystallized three times were stored under helium in closed vials (i) at —20° in darkness, (ii) at room temperature (20°) in darkness and (iii) at room temperature in daylight (not direct sunlight), respectively. Three more samples from the batch mentioned above were stored under 50 ml of air in analogous

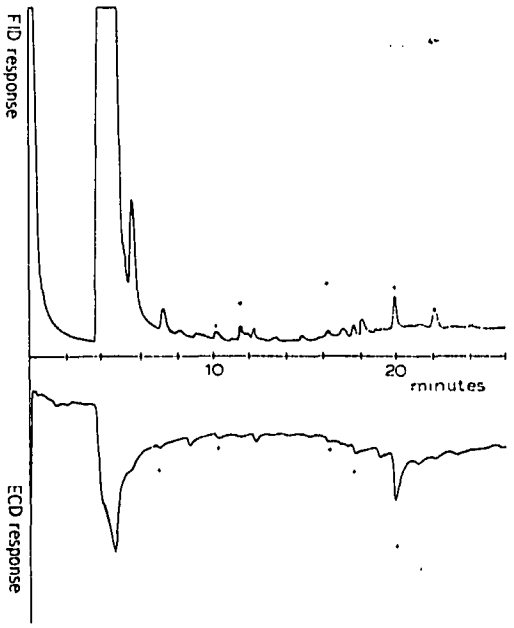

Fig. 2. Chemical signatures of high purity phenmetrazine hydrochloride. The dots indicate roughly the peak height changes observed after storage for 50 days at room temperature either under the influence of daylight (not direct sunlight) or in the presence of air. The anomalous peak appearing in the ECD signature at 4–6 min was caused by contamination of the ECD source.

conditions. After 50 days the six samples were analyzed and their signatures were compared with the original ones. A few peaks showed slightly increased heights in some cases. This effect was most pronounced at room temperature, either under the influence of daylight or in the presence of air. The change of the signatures in these cases, indicated in Fig. 2, may be due to a slight instability of phenmetrazine hydrochloride. However, in practice, illicit drugs will usually be kept in darkness and in capsules which reduce the headspace volume drastically. The change of the signatures will then be even less pronounced and should therefore not seriously affect the conclusions drawn from the analyses. This assumption was supported when phenmetrazine hydrochloride in capsules, seized on five different occasions, was analyzed. Their signatures did not show major peaks at the "critical" retention times. Phenmetrazine hydrochloride samples showing similar signatures may consequently be traced to a common source.

It may be assumed that chemical signatures can be obtained by GC of narcotic drugs other than those described above, and in the first and second parts of this series. Examples of signatures from seized crude morphine and heroin hydrochloride samples (purity around 90%) respectively, are shown in Figs. 3 and 4.

For synthetic narcotic drugs the inter-batch variations may be expected to be relatively large, due to the impurities of the starting material (which will vary) and to side reactions which will also vary with the experimental conditions of the synthesis.

The intra-batch variations of the chemical signatures may be expected to be

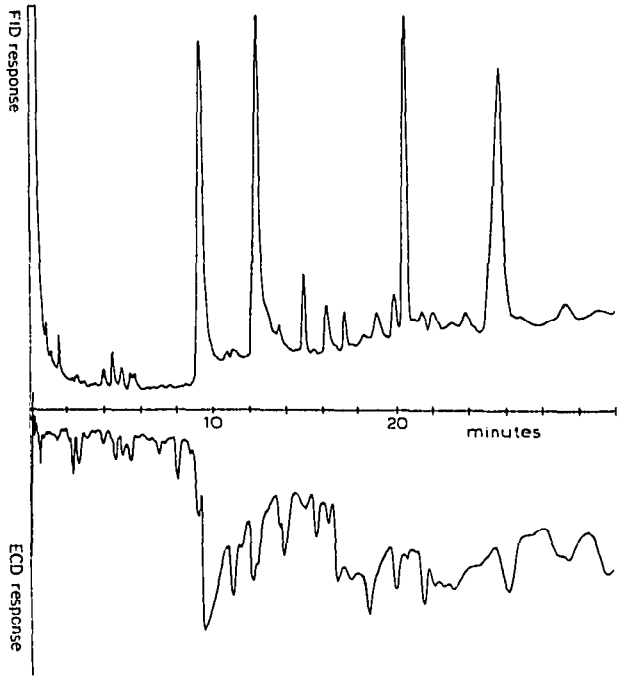

Fig. 3. Chemical signatures of a seized morphine sample. The experimental conditions were the same as in the case of phenmetrazine hydrochloride except that the aqueous layer was acidified to pH 3–4 in order to minimize the amount of co-extracted morphine.

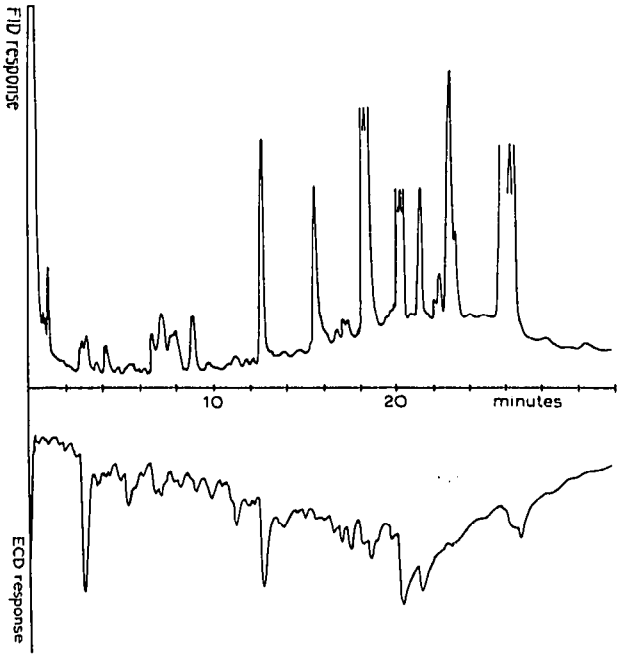

Fig. 4. Chemical signatures of a seized heroin hydrochloride sample. The experimental conditions were the same as in the case of phenmetrazine hydrochloride except that the aqueous layer was acidified to pH 3–4 in order to minimize the amount of co-extracted heroin.

relatively small for narcotics consisting of a single drug since these drugs are synthesized in liquid media.

Under these circumstances, tracing of samples of synthetic drugs to a common source may, as a rule, be carried out on the basis of their GC chemical signatures. A prerequisite for this is sufficient stability of the main constituents under normal storage conditions.

Special precautions should be taken concerning drug mixtures. Preliminary analyses carried out at this laboratory indicate that intra-batch variations are considerably larger in seized drug mixtures. This is not surprising since these products are prepared by mixing single-component drugs in their solid forms. The resulting variations in the intra-batch composition of such drug mixtures make the interpretation of the analyses difficult in some cases. At present, drug mixtures are frequently encountered on the illicit market of Sweden. Typical main constituents are amphetamine, methamphetamine, phendimetrazine, ephedrine and propyl hexedrine.

The possibility of external contamination must always be kept in mind when studying chemical signatures. The influence of this factor was discussed in Part II[2]. Clean glass vials should be used when sending samples to the laboratory for comparative analysis. The precautions necessary in connection with the analysis were mentioned under Experimental (above) and in Part II.

As pointed out above, the analyses should preferably be carried out in series lest the influence of changes in the performance of the GC system interfere. Such

changes may be due, for example, to column ageing or contamination of the ECD source.

ACKNOWLEDGEMENT

The authors wish to thank Miss May-Britt Larsson for her skilful assistance in connection with the GC analyses.

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